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(54) Title: STABLE WATERBORNE POLYMER COMPOSITIONS CONTAINING POLY(ALKYLENEIMINES)

(57) Abstract

This invention provides waterborne polymer compositions stabilized against gelling due to the addition of poly(alkyleneimine) by post addition of certain anionic surfactants. The waterborne polymer compositions of the invention are useful in a variety of coating formulations such as, for example, paints, inks, sealants, textile backcoatings, adhesives and the like. Methods of making stable waterborne polymer compositions are also disclosed.

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STABLE WATERBORNE POLYMER COMPOSITIONS CONTAINING POLY(ALKYLENEIMINES)

5 FIELD OF THE INVENTION

This invention belongs to the field of emulsion chemistry. In particular, it relates to stable waterborne polymer compositions useful in a variety of coating formulations.

10 BACKGROUND OF THE INVENTION

In an increasing number of industries, aqueous coating compositions continue to replace traditional organic solvent-based coating compositions. Paints, inks, sealants, and adhesives, for example, previously formulated with organic solvents are now formulated as aqueous compositions. This 15 reduces potentially harmful exposure to volatile organic compounds (VOC's) commonly found in solvent-based compositions. While the move from organic solvent-based to aqueous compositions brings health and safety benefits, the aqueous coating compositions must meet or exceed the performance standards expected from solvent-based compositions. The 20 need to meet or exceed such performance standards places a premium on the characteristics and properties of waterborne polymer compositions used in aqueous coating compositions.

Waterborne polymer having various functional groups have been used to impart and achieve desired properties to a particular coating 25 composition. For example, a coating composition should exhibit good film formation, print and block resistance, as well as adhesion and tensile properties. Polymers having acetoacetoxy- and enamine-functional groups represent one example of waterborne polymers which have such properties, may carry different functional groups, and are useful in aqueous 30 coating compositions.

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U.S. Patent 5,296,530 discloses a quick-curing coating prepared from a polymer having acetoacetyl groups, in which substantially all of the acetoacetyl groups have been converted to enamine functional groups. This conversion occurs, for example, by treatment with ammonia or a primary amine. Coatings so prepared cure more quickly under sunlight or ultraviolet light than coatings which contain the acetoacetyl functional polymer but which have not been converted to an enamine form.

U.S. Patents 5,484,975 and 5,525,662 describe the preparation of polymers containing functional acetoacetate groups and then, following the polymerization, reacting the acetoacetate group with a functional amine to form an enamine. The resulting polymers are reported to have a variety of uses including coatings, sealants, adhesives, and saturant applications.

U.S. Patent 5,498,659 discloses polymeric formulations comprising an aqueous carrier, at least one polymeric ingredient, a non-polymeric polyfunctional amine, and a base. The polymeric ingredient has both acid-functional and acetoacetoxy-type functional moieties. The aqueous polymeric formulations produce crosslinked polymeric surface coatings on a substrate.

Japanese Patent 61-21171 describes a fast-curing adhesive of two separate liquids. The first liquid is an aqueous solution and/or aqueous emulsion of a polymer compound containing an acetoacetyl group. The second liquid consists of polyethylenimine.

Even with current waterborne polymer formulations, a need remains for improved aqueous coating compositions and waterborne polymers for use in those compositions. In particular, a need exists for waterborne polymer compositions which may formulate as a single, stable composition but which undergo crosslinking upon film formation imparting one or more desired properties to the resulting coating. The present invention meets such needs.

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SUMMARY OF THE INVENTION

This invention provides stable waterborne polymer compositions which are stabilized against gelling upon addition of a poly(alkylenimine), preferably by post polymerization addition of certain anionic surfactants.

- 5 These stable waterborne polymer compositions are useful in a variety of coating formulations such as, for example, paints, inks, sealants, and adhesives. When used in coating formulations, the stable waterborne polymer compositions of the invention provide adhesion and crosslinking in the final film or coating. The film or coating may be cured at ambient
- 10 temperatures or may be thermally cured. Methods of preparing stable waterborne polymer compositions are also disclosed, along with methods of stabilizing latex compositions against gelling upon addition of a poly(alkylenimine).

15 DETAILED DESCRIPTION OF THE INVENTION

The present invention provides stable waterborne polymer compositions, that is compositions containing a polymer and water.

Waterborne polymer compositions include, but are not limited to, latexes, dispersions, microemulsions, or suspensions. Waterborne polymer

- 20 compositions of the present invention are stable and may be stored at room temperature or moderately above room temperature (e.g., about 50 to 60°C) and provide adhesion and crosslinking upon film formation when applied to a substrate. Yet, a film or coating formed with polymers of the invention may be cured at room temperature (ambient cure) or at elevated
- 25 temperatures (thermal cure).

The polymers used to prepare the waterborne polymer composition of the present invention are generally prepared as particles. The particles may be structured or unstructured. Structured particles include, but are not limited to, core/shell particles and gradient particles. The average polymer

- 30 particle size may range from about 25 to about 600 nm.

The polymer particles generally have a spherical shape. In one embodiment, the generally spherical polymeric particle may have a core portion and a shell portion. The core/shell polymer particles may also be prepared in a multilobe form, a peanut shell, an acorn form, or a raspberry form. It is further preferred in such particles that the core portion comprises about 20 to about 80 of the total weight of said particle and the shell portion comprises about 80 to about 20 of the total weight volume of the particle.

Although the following description will be directed to a discussion of specific types of polymers, other waterborne latex polymers that are susceptible to gelling upon addition of a poly(alkylenimine) are within the scope of the present invention.

Enamine-functional polymers represent a preferred embodiment of polymers used to form the stable waterborne polymer compositions of the present invention. Enamine-functional polymers may be prepared by reacting a polymer having acetoacetoxy groups with ammonia or a primary or secondary amine. The primary or secondary amine may be a monoamine compound or a polyamine compound. Preferred amines include, for example, triaminononane, $H_2N(CH_2)_3CH(CH_2NH_2)(CH_2)_4NH_2$ (CAS Registry No. 1572-55-0), available from Monsanto; 2-amino-2-methyl-1-propanol available as AMP-95 product from Angus Chemical Company, Buffalo Grove, IL; or, as described below, polyethylenimine (PEI). In water-based latexes, the enamine functionality serves to further stabilize the acetoacetoxy-groups and protect them from hydrolysis. Enamine-functional polymers have been described in Moszner et al., Polymer Bulletin 32, 419-426 (1994); European patent Application No. 0 492 847 A2; U.S. Patent No. 5,296,530; and U.S. Patent No. 5,484,849. These documents are incorporated herein by reference.

Acetoacetoxy-type functional polymers useable in the present invention may be prepared by free radical emulsion polymerization of vinyl monomers having an acetoacetoxy functionality such as those of

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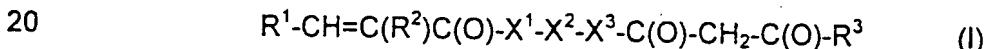
Formula (I) below with other vinyl monomers. This combination of monomers provides water-based dispersion of polymer particles where the polymer has pendant acetoacetoxy groups. As used here, a "vinyl" monomer is an ethylenically unsaturated monomer. A pendant

- 5 acetoacetoxy group is not strictly limited to those at the termini of the polymer. Pendant acetoacetoxy groups also include groups attached to the polymer's backbone and available for further reaction.

Acetoacetoxy-type functional polymers preferably contain about 0.5 to about 30 weight percent of vinyl monomers having acetoacetoxy-type

- 10 functionality such as those of Formula I, and about 99.5 to about 70 weight percent of other vinyl monomers, preferably alkyl (meth)acrylates having 1 to 18 carbons. The weight percentage is based on the total amount of monomers in the composition. More preferably, the stabilized polymer has about 1 to about 15 weight percent acetoacetoxy monomers, and about 99
15 to about 85 weight percent of other vinyl monomers.

Aspects of this emulsion polymerization and preferred embodiments are discussed below beginning with vinyl monomers as in Formula (I) which have an acetoacetoxy-type functionality.



- For an acetoacetoxy-type monomer of Formula (I), R^1 is a hydrogen or halogen. R^2 is a hydrogen, halogen, $C_1\text{-}C_6$ alkylthio group, or $C_1\text{-}C_6$ alkyl group. R^3 is a $C_1\text{-}C_6$ alkyl group. X^1 and X^3 are independently O, S, or a group of the formula $\text{-N}(R')-$, where R' is a $C_1\text{-}C_6$ alkyl group. X^2 is a $C_2\text{-}C_{12}$ alkylene group or $C_3\text{-}C_{12}$ cycloalkylene group. The alkyl and alkylene groups described here and throughout the specification may be straight or branched groups. Preferred monomers of Formula (I) are acetoacetoxyethyl methacrylate, acetoacetoxyethyl acrylate,
30 acetoacetoxy(methyl)ethyl acrylate, acetoacetoxypropyl acrylate, allyl

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acetoacetate, acetoacetamidoethyl (meth)acrylate, and acetoacetoxybutyl acrylate. Acetoacetoxyethyl methacrylate (AAEM) represents a particularly preferred monomer of Formula (I).

- Suitable other vinyl monomers which may be reacted with the vinyl monomers having acetoacetoxy-type functionality include, but are not limited to, methyl acrylate; methyl methacrylate; ethyl acrylate; ethyl methacrylate; butyl acrylate; butyl methacrylate; isobutyl acrylate; isobutyl methacrylate; ethylhexyl acrylate; ethylhexyl methacrylate; octyl acrylate; octyl methacrylate; styrene; α -methyl styrene; glycidyl methacrylate; carbodiimide methacrylate; C₁-C₁₈ alkyl crotonates; di-n-butyl maleate; dioctylmaleate; allyl methacrylate; di-allyl maleate; di-allylmalonate; methoxybutenyl methacrylate; isobornyl methacrylate; hydroxybutenyl methacrylate; hydroxyethyl (meth)acrylate; hydroxypropyl (meth)acrylate; acrylonitrile, vinyl chloride; ethylene; methacrylamide; acrylamide; butyl acrylamide; ethyl acrylamide; vinyl (meth)acrylate; isopropenyl (meth)acrylate; cycloaliphatic epoxy (meth)acrylates; and ethylformamide. Such monomers are described in "The Brandon Worldwide Monomer Reference Guide and Sourcebook" Second Edition, 1992, Brandon Associates, Merrimack, New Hampshire; and in "Polymers and Monomers", the 1996-1997 Catalog from Polyscience, Inc., Warrington, Pennsylvania.

Vinyl esters of the general Formula (II) represent further examples of useful other vinyl monomers:



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- In Formula (II), R is independently hydrogen or an alkyl group of up to 12 carbon atoms. Particular monomers of Formula (II) include CH₂=CH-O-C(O)-CH₃, CH₂=CH-O-C(O)-C(CH₃)₃, CH₂=CH-O-C(O)-CH(C₂H₅)(C₄H₉), and CH₂=CH-O-C(O)-CH₂CH₃. Vinyl ester monomers also include vinyl esters of vinyl alcohol such as the

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VEOVA series available from Shell Chemical Company as VEOVA 5, VEOVA 9, VEOVA 10, and VEOVA 11 products. See O.W. Smith, M.J. Collins, P.S. Martin, and D.R. Bassett, Prog. Org. Coatings 22, 19 (1993).

Optional monomers that may be incorporated into the polymer

- 5 include styrene, butyl styrene, vinyl toluene, α -methyl styrene, (meth)acrylamide, (meth)acrylonitrile, vinyl acetate, and vinyl esters of acids other than acetic acid, itaconic anhydride, maleic anhydride, vinyl formate, and salts of 2-sulfoethyl (meth)acrylate.

In one embodiment, the acetoacetoxy functional polymer may also

- 10 incorporate nitrogen-containing, vinyl monomers known to promote wet adhesion. Exemplary wet adhesion monomers include, for example, t-butylaminoethyl methacrylate; dimethylaminoethyl methacrylate; diethylaminoethyl methacrylate; N,N-dimethylaminopropyl methacrylamide; 2-t-butylaminoethyl methacrylate; N,N-dimethylaminoethyl acrylate;
- 15 N-(2-methacrylamido-ethyl)ethylene urea; and N-(2-methacryloyloxyethyl)ethylene urea. N-(2-methacryloyloxyethyl)ethylene urea is available from RohmTech as 50% solution in water under the Rohamere 6852-O trade name and as a 25% solution in water under the Rohamere 6844 trade name. N-(2-methacrylamido-ethyl)ethylene urea is available from Rhone-Poulenc under the WAM trade name.

Small amounts of acid vinyl monomers may also be used to prepare acetoacetoxy emulsion polymers according to the invention. Such acid vinyl monomers include, for example, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, and 2-acrylamido-2-methyl-1-

- 25 propanesulfonic acid (sodium, potassium, or ammonium salts). Incorporating acid vinyl monomers into the stabilized polymer may increase the viscosity of the resulting latex and may have a detrimental effect on the formation of an enamine-functional polymer according to the invention.

Generally these monomers are used in small amounts. Preferably, the

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amount of acid vinyl monomers may range, for example, from 0 to 5 phr. Larger amounts of acid vinyl monomers may be used to achieve a desired effect, such as increased viscosity.

- The acetoacetoxy polymer may be prepared using emulsion
- 5 polymerization techniques known in the art. The acetoacetoxy polymer may, as is known in the art, be prepared using free radical emulsion polymerization techniques which yield structured or unstructured particles. As mentioned above, structured particles include, for example, core/shell particles, raspberry particles, and gradient particles. Chain transfer agents,
- 10 initiators, reducing agents, catalysts, and surfactants known in the art of emulsion polymerization, may be used to prepare the polymers.

Chain transfer agents may optionally be added, in an amount up to about 2 weight percent based on total monomer content, to control the molecular weight of the polymer. Use of chain transfer agents may be

15 preferred when it is desired to obtain low molecular weight polymers.

Exemplary chain transfer agents are butyl mercaptan, mercaptopropionic acid, 2-ethylhexyl mercaptopropionate, dodecylmercaptan, n-butyl mercaptopropionate, octyl mercaptan, isodecyl mercaptan, octadecyl mercaptan, mercaptoacetic acid, allyl mercaptopropionate, allyl mercapto-

20 acetate, crotyl mercaptopropionate, crotyl mercaptoacetate, and the reactive chain transfer agents taught in U.S. Patent No. 5,247,040, incorporated here by reference. In particular, 2-ethylhexyl mercapto-propionate and dodecylmercaptan represents preferred chain transfer agents.

25 Typical initiators include hydrogen peroxide, sodium, potassium or ammonium peroxydisulfate, dibenzoyl peroxide, lauryl peroxide, tertiary butyl peroxide, 2,2'-azobisisobutyronitrile, t-butyl hydroperoxide, benzoyl peroxide, and the like.

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Suitable reducing agents are those which increase the rate of polymerization and include for example, sodium bisulfite, sodium hydrosulfite, sodium formaldehyde sulfoxylate, ascorbic acid, isoascorbic acid, and mixtures thereof.

- 5 Polymerization catalysts are those compounds which increase the rate of polymerization and which, in combination with the above described reducing agents, may promote decomposition of the polymerization initiator under the reaction conditions. Suitable catalysts include transition metal compounds such as, for example, ferrous sulfate heptahydrate, ferrous chloride, cupric sulfate, cupric chloride, cobalt acetate, cobaltous sulfate, and mixtures thereof. Peroxide-iron and peroxide-sulfite redox catalysts may also be used.
- 10

Crosslinking agents may optionally be added, in an amount up to about 2 weight percent, based on total monomer content, to control the 15 molecular weight of the polymer. Use of crosslinking agents may be preferred when it is desired to obtain high molecular weight polymers. Useful crosslinkers include trimethylopropane tri(meth)acrylate, 1,6-hexanediol di(meth)acrylate, allyl methacrylate and the like.

- 20 Any conventional polymerization surfactant may be used to form the polymer of the present invention. Useful surfactants include, but are not limited to, ionic and nonionic surfactants such as alkyl polyglycol ethers; alkyl phenol polyglycol ethers; alkali metal ammonium salts of alkyl, aryl or alkylaryl sulfonates, sulfates, phosphates, and the like, and reactive anionic or nonionic surfactants possessing styrene or allyl groups. Sulfonate 25 containing surfactants such as sodium dodecyl benzene sulfonate, sodium dodecyl sulfate, or the diesters of sodiosulfosuccinic acid such as sodium dioctylsulfo-succinate, and alpha olefin sulfonates are suitable. When persulfate catalysts are used, in-situ-generated oligomers with sulfate end groups may act as surfactants.

- 10 -

Although the above list of useful surfactants may include some of the same surfactants listed below for post-polymerization addition, incorporation of these particular surfactants into the polymerization process has not been found to stabilize the polymer against gelling upon addition of 5 poly(alkylenimine) and upon adjusting the pH of the polymer.

The type and amount of surfactant used in the polymerization process depends on the specific composition, reaction conditions, and the desired final particle size, as is known in the art.

Water-dispersible and water-soluble polymers may also be employed 10 as surfactants/stabilizers in the water-based latexes of the invention. Examples of such polymeric stabilizers include water-dispersible polyesters as described in U.S. Patent Nos. 4,946,932 and 4,939,233; water-dispersible polyurethanes as described in U.S. Patent Nos. 4,927,876 and 5,137,961; alkali-soluble acrylic resins as described in U.S. Patent No. 15 4,839,413; and hydroxyethyl cellulose, as described in U.S. Patent No. 3,876,596 and British Patent 1,155,275.

The acetoacetoxy functionality in the polymer may be present as free acetoacetoxy groups or as derivatives of those groups such as, for example, an enamine group or acetoacetamide group. The acetoacetoxy- 20 functional polymer may contain both free acetoacetoxy groups and acetoacetoxy derivatives.

As discussed above, enamine-functional polymers may be prepared by addition of a primary or secondary amine to the acetoacetoxy polymer. Preferred amines are poly(alkylenimines). Poly(alkylenimines) for use in 25 the invention may have a weight average molecular weight of about 800 to about 750,000. The poly(alkylenimine) is preferably a polyethylenimine (PEI) and more preferably PEI having a weight average molecular weight of about 800 to about 25,000. The PEI may contain primary, secondary, and tertiary amine groups, for example, in a ratio of 1.5:1.4:1.0, respectively. 30 Such PEI compounds are commercially available from BASF Corporation

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as LUPASOL™ G-35 polyethylenimine. Depending on the requirements of the end-use of the formulation, the content of polyethylenimine can vary from 0.5 to 25 weight percent based on the dry weight of the acetoacetoxy polymer. More preferably, the content of polyethylenimine can vary from 2

5 to 12 weight percent based on the dry weight of the acetoacetoxy polymer.

However, poly(alkylenimines), particularly polyethylenimine, are known to flocculate latexes, and are actually sold for that purpose. The pH of the prepared latex is normally greater than 11, much too high for many commercial applications. After addition of a poly(alkylenimine), upon

10 adjustment of the pH of the latex to a pH of less than about 10, the latex normally gels.

It has been unexpectedly found that the thus formed enamine polymers may be stabilized against gelling due to the addition of poly(alkylenimine), by post polymerization addition of a surfactant.

15 Preferably the surfactant is an anionic surfactant selected from salts of phosphate or sulfate esters of alkyl or alkylaryl ethoxylates containing at least five EO units. Useful anionic surfactants include, but are not limited to, ammonium, amine, sodium, potassium, and lithium salts of the above compounds such as ammonium salts of sulfated alkyl phenol ethoxylates,

20 sodium napthalene sulfonate formaldehyde polymers, phosphated octyl phenol ethoxylates and aromatic phosphate esters. Preferred anionic surfactants for use in the present invention are Aerosol NPES 930P

surfactant available from Cytech Industries, Daxad 19 surfactant available from W.R. Grace and Company, Triton QS-44 surfactant available from

25 Union Carbide Corporation, and Maphos 6600 surfactant available from PPG Industries. In contrast to polymers that flocculate upon addition of a poly(alkylenimine), the addition of a poly (alkyleneimine), particularly polyethylenimine, to polymers to which these anionic surfactants has been added, does not cause flocculation, but provides a stable, waterborne

30 polymer composition.

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The addition of polyethylenimine may be accomplished by adding, with stirring, polyethylenimine to an emulsion of the acetoacetoxy polymer to which has also been added an anionic surfactant as described above. Sufficient surfactant should be added to stabilize the enamine polymer.

- 5 Typically, the surfactant may be added in an amount of from about 0.5 phr to about 5 phr based on dry polymer weight. Optionally, the surfactant may be added, with stirring, with the polyethylenimine or after addition of the poly(ethyleneimine); but prior to adjusting the pH of the polymer. Other surfactants and property modifying ingredients may also be added that do not impact on the stability of the waterborne composition.
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 - 20
- The pH of the stable waterborne enamine polymer of the invention may then be adjusted by the addition of an acid or buffer. For example, buffers such as sodium bicarbonate, ammonium bicarbonate, ammonium dihydrogenphosphate, an ammonium polyacrylate, or a mixture of such buffers may be used. The buffer, such as ammonium bicarbonate, may generally be added to the stable, waterborne enamine polymer to adjust and/or buffer the pH of the composition to less than about 10. Waterborne enamine polymer compositions having pH values in the range of about 7.0 to about 9.8, preferably about 8.4 to about 9.2, may be achieved using ammonium buffers. Buffered compositions of the invention are particularly useful in coating formulations.

- 25
- The stable enamine polymers of the present invention will vary in properties, depending on the end-use application. In general, the polymer composition may have a second cycle glass transition temperature (T_g) of -50 to +100°C; more preferably, -35 to +50°C.

The weight average molecular weight of the stable enamine polymers may vary from about 20,000 to 5,000,000 daltons; more preferably from 100,000 to 2,000,000 and most preferably from 200,000 to

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1,000,000. The molecular weight range may be controlled by reaction conditions, as is known in the art, or by the use of a chain transfer agent or crosslinkers, as discussed above.

A waterborne polymer composition of the invention may also contain 5 other additives known in those compositions and may use other emulsion polymerization methodology. U.S. Patent No. 5,371,148 provides a good description of possible additives and is incorporated herein by reference.

In a waterborne composition of the invention, the stable acetoacetoxy-functional, or enamine-functional polymers, may be present 10 from about 5 to about 60 weight percent based on dry resin and more preferably from about 25 to about 55 weight percent. The examples below illustrate the preparation of polymers and water-based compositions according to the invention.

Latexes or other water-based compositions containing small particle 15 size polymers, those ranging from about 25 to about 100 nm and more preferably from about 45 to about 85 nm, represent one preferred embodiment of the invention.

The stable polymers and waterborne polymer compositions of the invention are useful in a variety of coating formulations such as architectural 20 coatings, metal coatings, wood coatings, plastic coatings, textile coatings, cementitious coatings, paper coatings, inks, and adhesive. Examples of such coating formulations adapted for particular uses include, but are not limited to, corrosion inhibitors, concrete coatings, maintenance coatings, latex paints, industrial coatings, automotive coatings, textile backcoatings, 25 surface printing inks and laminating inks. Accordingly, the present invention relates to such coating formulations containing a waterborne polymer composition of the invention, preferably a water-based latex. The polymers and waterborne polymer compositions of the invention may be incorporated in those coating formulations in the same manner as known polymer

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5 latexes and used with the conventional components and or additives of such compositions. The coating formulations may be clear or pigmented. With their crosslinking ability, adhesion properties, and resistance properties, the water-based latexes of the invention impart new and/or improved properties to the various coating formulations.

Upon formulation, a coating formulation containing a stable polymer or waterborne polymer composition of the invention may then be applied to a variety of surfaces, substrates, or articles, e.g., paper, plastic, steel, aluminum, wood, gypsum board, concrete, brick, masonry, or galvanized 10 sheeting (either primed or unprimed). The type of surface, substrate, or article to be coated generally determines the type of coating formulation used. The coating formulation may be applied using means known in the art. For example, a coating formulation may be applied by spraying or by coating a substrate. In general, the coating may be dried by heating but 15 preferably is allowed to air dry. Advantageously, a coating employing a polymer of the invention may be thermally or ambiently cured. As a further aspect, the present invention relates to a shaped or formed article which has been coated with a coating formulations of the present invention.

A waterborne polymer composition according to the invention may 20 comprise the stabilized polymer of the invention and water, along with a solvent, a pigment (organic or inorganic) and/or other additives and fillers known in the art, and enumerated below. When a solvent is used, water-miscible solvents are preferred. A latex paint composition of the invention may comprise a waterborne polymer composition of the invention, a 25 pigment and one or more additives or fillers used in latex paints.

Additives or fillers used in formulating coatings include, but are not limited to, leveling, rheology, and flow control agents such as silicones, fluorocarbons, urethanes, or cellulosics; extenders; curing agents such as multifunctional isocyanates, multifunctional carbonates, multifunctional 30 epoxides, or multifunctional acrylates; reactive coalescing aids such as

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- those described in U.S. Patent No. 5,349,026; flattening agents; pigment wetting and dispersing agents and surfactants; ultraviolet (UV) absorbers; UV light stabilizers; tinting pigments; extenders; defoaming and antifoaming agents; anti-settling, anti-sag and bodying agents; anti-skinning agents;
- 5 anti-flooding and anti-floating agents; fungicides and mildewcides; corrosion inhibitors; thickening agents; plasticizers; reactive plasticizers; drying agents; catalysts; crosslinking agents; or coalescing agents. Specific examples of such additives can be found in Raw Materials Index, published by the National Paint & Coatings Association, 1500 Rhode Island Avenue,
- 10 NW, Washington, D.C. 20005.

A polymer or waterborne polymer composition of the present invention can be utilized alone or in conjunction with other conventional waterborne polymers. Such polymers include, but are not limited to, water dispersible polymers such as consisting of polyesters, polyester-amides, cellulose esters, alkyds, polyurethanes, epoxy resins, polyamides, acrylics, vinyl polymers, polymers having pendant allyl groups such as described in U.S. Patent No. 5,539,073, styrene-butadiene polymers, vinylacetate-ethylene copolymers, and the like.

15

The following examples are intended to illustrate, not limit, the invention:

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EXAMPLES

Example 1:

Latex Synthesis:

- 5 The reactor configuration was a 4 liter jacketed kettle held at 80°C with circulating water. Deionized water was used and the atmosphere above the reaction was inerted with nitrogen. The reactor was charged with 1000 g water, 3 g of sodium bicarbonate and 54.5 g (1.5 phm) of Rhodacal A246L surfactant (a C_{12,14} alpha olefin sodium sulfonate surfactant
- 10 available from Rhone-Poulenc as a 38.5% solution in water), and heated to 80°C. An emulsion was made with 700 g of water, 10.9 g (0.3 phm) of Rhodacal A246L surfactant, 672 g of styrene, 476 g of butyl acrylate, 70 g of 2-hydroxyethyl methacrylate (HEMA), 140 g of acetoacetoxyethyl methacrylate (AAEM) and 84 g of sodium 2-acrylamido-2-methylpropane
- 15 sulfonate (AMPS 2405 monomer, available from Lubrizol Corporation as a 50% solution in water). To the reactor was added 110 g of the above emulsion, followed by a solution of 2.7 g of sodium persulfate in 20 g of water. After 5 minutes, the remainder of the emulsion was fed to the reactor over a 2 hour period. At the same time a solution of 1.5 g of sodium
- 20 persulfate in 50 g of water was added to the reactor over a 1 hour period. The reaction mixture was held at 80°C for 30 minutes after addition was complete, and the reactor was then cooled. As the reactor was cooled, a solution of 1.5 g of t-butylhydroperoxide in 30 g of water was added rapidly through the emulsion feed, and a solution of 1.5 g of sodium metabisulfite,
- 25 1.0 g of 50% sodium hydroxide solution and 80 g of water was added over 30 minutes. The pH of the latex was 7.36, particle size was 74 nm, and had 42.1% solids.

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Addition of PEI:

- A mixture of 336 g of a 40% solution of LUPASOL™ G-35 polyethylenimine (a 50% solids product of BASF) in water, 60 g of Aerosol NPES 930P surfactant (available from Cytech Industries), and 84 g of water was added to the reactor over 30 minutes with a sub-surface feed. The pH of the latex was 11.2 and the particle size was 81 nm.
- 5

pH Adjustment

- 10 After 15 minutes a solution of 5% ammonium carbonate and 15% ammonium bicarbonate in water was added (550 g) to achieve a pH of 9.84. The entire batch filtered rapidly through a 40 mm, 100 mesh stainless steel screen. The pH of the latex was 9.84, the particle size was 80 nm, and percent solids was 37.25%. This latex showed no significant thickening
- 15 after 2 weeks at 60°C.

Example 2 - Comparative Example:

- 100 g of the latex similar of Example 1 was treated with the same proportion of PEI, but without post polymerization addition of Aerosol NPES
- 20 930P surfactant, adjusting the pH of the latex to 9.8 caused the mixture to gel within ten minutes.

Example 3: - Evaluation of Various Anionic Surfactants

- The latex of Example 1 was used to evaluate various anionic surfactants. To 3270 g of this latex was added 330 g of a 40% solution of LUPASOL™ G-35 polyethylenimine in water (a 50% solids product of BASF). The particle size of the latex was 80 nm.
- 25

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This mixture was then blended with various anionic surfactants at the rate of 3 g of surfactant (active basis) per 100 g of polymer (dry basis) and pH adjusted to 9.8 with a solution of 5% ammonium carbonate and 15% ammonium bicarbonate. The viscosity of the product was estimated by hand over time. The results with various anionic surfactants are shown in Table 1.

TABLE 1 - Anionic Surfactants

Surfactant	Type	Class	RESULT UPON pH ADJUSTMENT to pH 9.8
None (Ex. 2)	None	None	Gelled immediately
sodium dodecyl sulfate	alcohol sulfate	Anionic	Gelled immediately
sodium dodecylbenzene sulfonate	alkylbenzene sulfonate	Anionic	Gelled immediately
Aerosol® OT-75	sodium bis(2-ethylhexyl)sulfosuccinate	Anionic	Gelled immediately
Rhodapex CO-436	ammonium salt of a sulfated alkyl phenol ethoxylate with 4 EO units	Anionic	Gelled immediately
Aerosol NPES 930P	ammonium salt of a sulfated alkyl phenol ethoxylate with 30 EO units	Anionic	Stable at 60°
Rhodacal® A246L	alpha olefin sulfonate, sodium salt	Anionic	Gelled 10 minutes
potassium oleate	soap	Anionic	Gelled immediately
Igepon® T-51	Sodium N-methyl-N-oleoyl taurate	Anionic	Gelled immediately
DowFax 2A1	Sodium dodecyl diphenyloxide disulfonate	Anionic	Gelled immediately

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Daxad® 19	sodium naphthalene sulfonate - formaldehyde polymer	Anionic	Stable at 60°
Triton QS-44	Phosphated octyl phenol ethoxylate	Anionic	Stable at 60°
Naxonac 600	Alcohol ether phosphate	Anionic	Gelled 5 minutes
Naxonac 610	Nonylphenol ether phosphate	Anionic	Gelled 5 minutes
Maphos 8135	Aromatic phosphate ester	Anionic	Gelled 5 minutes
Maphos 60A	Aliphatic phosphate ester	Anionic	Gelled 15 minutes
Maphos 30	Aliphatic phosphate ester	Anionic	Gelled 15 minutes
Maphos 6600	Aromatic phosphate ester	Anionic	Stable at 60°

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CLAIMS

What is claimed is:

1. A stable waterborne polymer composition comprising a polymer; a poly(alkylenimine); and an anionic surfactant selected from the group consisting of ammonium salts of sulfated alkyl phenol ethoxylates; sodium napthalene sulfonate formaldehyde polymers; phosphated octyl phenol ethoxylates and aromatic phosphate esters.
5
2. The stable waterborne polymer composition of claim 1
10 wherein said polymer comprises the reaction product of about 0.5 to about 30 weight percent of vinyl monomers having acetoacetoxy-type functionality of Formula (I):
15
3. The stable waterborne polymer composition of claim 2
10 where R¹ is a hydrogen or halogen; R² is a hydrogen, halogen, C₁-C₆ alkylthio group, or C₁-C₆ alkyl group; R³ is a C₁-C₆ alkyl group; X¹ and X³ are independently O, S, or a group of the formula -N(R')-, in which R' is a C₁-C₆ alkyl group; X² is a C₁-C₁₂ alkylene group or C₃-C₁₂ cycloalkylene group; and
20 about 99.5 to about 70 weight percent of other vinyl monomers.
about 99.5 to about 70 weight percent of other vinyl monomers.
4. The stable waterborne polymer composition of claim 2
25 wherein said vinyl monomer having acetoacetoxy-type functionality is selected from the group consisting of acetoacetoxy-ethyl methacrylate, acetoacetoxyethyl acrylate, acetoacetoxy(methyl)ethyl acrylate, acetoacetoxypropyl acrylate, allyl acetoacetate, acetoacetamidoethyl (meth)acrylate, and acetoacetoxybutyl acrylate.

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4. The stable waterborne polymer composition of claim 1 wherein said polymer further comprises up to about 2 weight percent of a chain transfer agent selected from the group consisting of butyl mercaptan, mercaptopropionic acid, 2-ethylhexyl mercaptopropionate,
5 dodecylmercaptan, n-butyl mercaptopropionate, octyl mercaptan, isodecyl mercaptan, octadecyl mercaptan, mercaptoacetic acid, allyl mercaptopropionate, allyl mercaptoacetate, crotyl mercaptopropionate, and crotyl mercaptoacetate; and up to about 2 weight percent of a crosslinking agent selected from the group consisting of trimethylol-propane
10 tri(meth)acrylate, 1,6-hexanediol di(meth)acrylate, and allyl methacrylate.

5. The stable waterborne polymer composition of claim 1 wherein said poly(alkylenimine) is present in an amount from about 0.5 to about 25 weight percent based on the dry weight of the polymer.
15

6. The stable waterborne polymer composition of claim 1 wherein said poly(alkylenimine) is poly(ethyleneimine).

7. A coating formulation selected from an architectural coating, a metal coating, a wood coating, a plastic coating, a textile coating, a cementitious coating, a paper coating, an ink, and an adhesive, comprising the stable waterborne polymer composition of claim 1 and at least one additive selected from a solvent, a pigment, a buffer, a leveling agent, a rheology agent, a curing agent, a flow control agent, an extender, a reactive coalescing aid, a flattening agent, a pigment wetting agent, a dispersing agent, a surfactant, an ultraviolet (UV) absorber, a UV light stabilizer, a defoaming agent, an antifoaming agent, an anti-settling agent, an anti-sag agent, a bodying agent, an anti-skimming agent, an anti-flooding agent, an anti-floating agent, a fungicide, a mildewcide, a corrosion inhibitor, a
20
25

thickening agent, a plasticizer, a reactive plasticizer, a drying agent, a catalyst, a crosslinking agent, and a coalescing agent.

8. A method of making a stable waterborne polymer composition
5 comprising polymerizing a vinyl monomer having an acetoacetoxy functionality with other vinyl monomers to form a polymer; adding a poly(alkylenimine) and an anionic surfactant selected from the group consisting of ammonium salts of sulfated alkyl phenol ethoxylates, sodium naphthalene sulfonate formaldehyde polymers, phosphated octyl phenol
10 ethoxylates and aromatic phosphate esters to said polymer; and adjusting the pH of the waterborne polymer composition to less than about 10.

9. The method of claim 8 wherein said polymer comprises the reaction product of about 0.5 to about 30 weight percent of vinyl monomers
15 having acetoacetoxy-type functionality and about 99.5 to about 70 weight percent of other vinyl monomers; said poly(alkylenimine) is polyethylenimine present in an amount from about 0.5 to about 25 weight percent based on the dry weight of the polymer; and the pH is adjusted in the range of from about 7.0 to about 9.8.
20

10. The method of claim 8 wherein said vinyl monomer having acetoacetoxy-type functionality is selected from the group consisting of acetoacetoxy-ethyl methacrylate, acetoacetoxyethyl acrylate, acetoacetoxy(methyl)ethyl acrylate, acetoacetoxypropyl acrylate, allyl
25 acetoacetate, acetoacetamidoethyl (meth)acrylate, and acetoacetoxybutyl acrylate.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/18609

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D5/02 C08L101/00 // (C08L101/00, 79:02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 980 404 A (AYDIN ORAL ET AL) 25 December 1990 see column 4	1
X	WO 96 22338 A (DOW CHEMICAL CO ;HELMER BRADLEY J (US); YOUNG JAMES W JR (US)) 25 July 1996 see example 1	1
X,P	WO 97 45468 A (EASTMAN CHEM CO) 4 December 1997 see page 11, line 7 - line 9	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search	Date of mailing of the international search report
4 January 1999	12/01/1999
Name and mailing address of the ISA European Patent Office, P.O. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer Schueler, D

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 98/18609

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 4980404	A	25-12-1990	DE	3642485 A	23-06-1988
			AU	597131 B	24-05-1990
			AU	8245987 A	16-06-1988
			CA	1318065 A	18-05-1993
			DE	3778505 A	27-05-1992
			EP	0271033 A	15-06-1988
			JP	63156876 A	29-06-1988
WO 9622338	A	25-07-1996	AU	693002 B	18-06-1998
			AU	4857896 A	07-08-1996
			BR	9606771 A	06-01-1998
			CA	2210807 A	25-07-1996
			CN	1168152 A	17-12-1997
			CZ	9702234 A	14-01-1998
			EP	0804514 A	05-11-1997
			FI	973038 A	17-07-1997
			PL	321464 A	08-12-1997
WO 9745468	A	04-12-1997	AU	3212297 A	05-01-1998
			AU	3212397 A	05-01-1998
			AU	3285997 A	05-01-1998
			WO	9745490 A	04-12-1997
			WO	9745495 A	04-12-1997